Low temperature oxidation of uranium dioxide

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Introduction and objective

The U-O system has been under investigation already since many decades. Continuation of such research is necessary due to its complexity, with renewed insights improving the front and back end of the UO_2 fuel cycle. Fuel manufacturing involves the handling of powders which present a risk for pyrophoricity under oxidizing conditions. Also, oxidation to the thermodynamically more stable oxide U_3O_8 results in a 36% volume expansion. Such a scenario can be detrimental for fuel cladding integrity (cf. storage and accidents of spent fuel).

Experimental research on the **kinetics** of UO_2 oxidation
1. Effect of oxidizing atmosphere
2. Effect of temperature, time (Figure 1)
3. Effect of particle properties (surface area)

Application of reaction **mechanisms**
1. Surface chemistry
2. Solid state chemistry
3. Crystallographic changes (Figure 2)

Oxidation kinetics

- Simultaneous Thermal Analysis (STA)
- Gas adsorption analysis (BET-theory)

Reaction mechanisms

- X-ray diffraction (XRD)
- Selected Area Electron Diffraction (SAED)
- Transmission Electron Microscopy (TEM)

Objective: Relate features at the *nano-* and *micro-scale* to the observed *macro* behaviour of UO_2 powders.

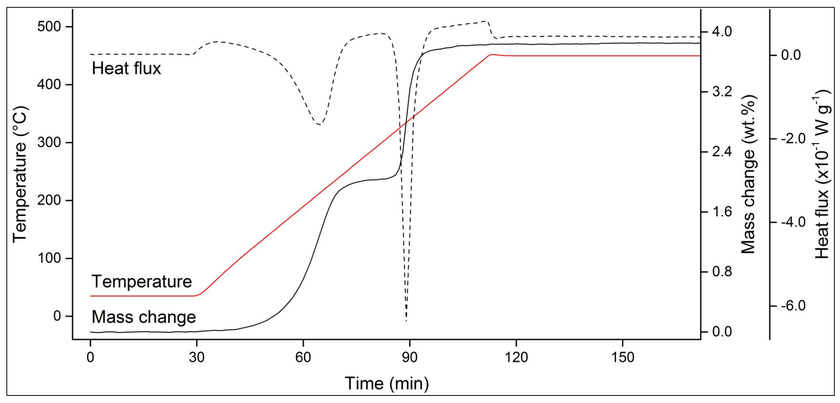


Figure 1. STA curve showing a two-stage reaction in the oxidation of UO_2 to U_3O_8.

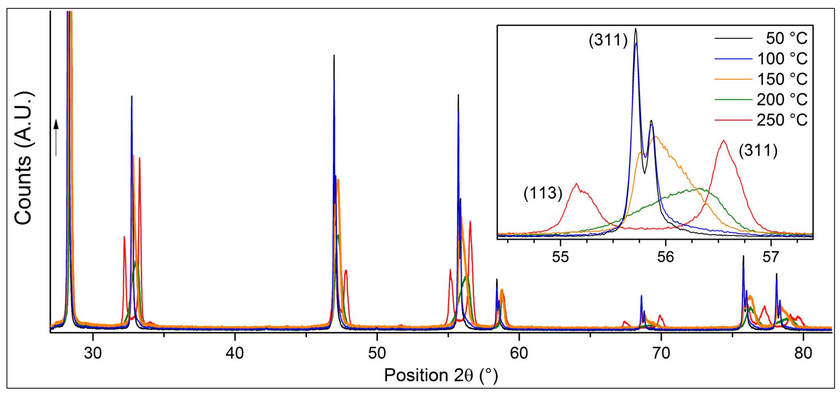


Figure 2. X-ray diffractograms of UO_2 oxidized at various temperatures for 7 h in dry air.

Results

$$UO_2\ (O/U = 2) \rightarrow UO_{2+x}\ (O/U = 2+x) \rightarrow \beta\text{-}U_4O_{9\pm y}\ (O/U = 2.25 \pm y) \rightarrow \beta\text{-}U_3O_7\ (O/U \approx 2.33) \rightarrow U_3O_8\ (O/U = 2.67)$$

Reaction mechanisms: crystallography

- UO_2: Fluorite structure ($Fm\bar{3}m$) with large interstitial holes

  a_0 = 547.127 ± 0.008 pm [1]

- UO_{2+x}: Oxygen take-up in interstitial positions results in lattice contraction

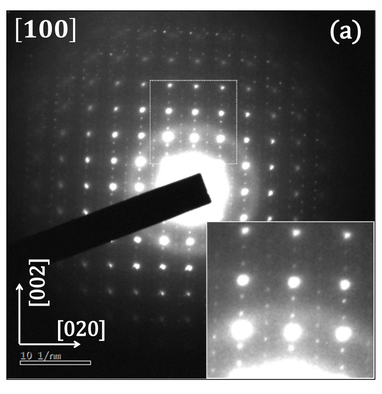
  $a_x = a_0 - (O/U - 2) \times 9.4$ pm [2]

- β-$U_4O_{9\pm y}$: Long-range coordination of oxygen defect clusters in a $4a \times 4a \times 4a$ superstructure [3]

  $a = 4 \times 544.0$ pm

- β-U_3O_7: Increased oxygen take-up results in tetragonal deformation and *modulation* within the basic structure (Figure 3 (a, b))

  a = 538.21 ; c = 555.16 ± 0.01 pm



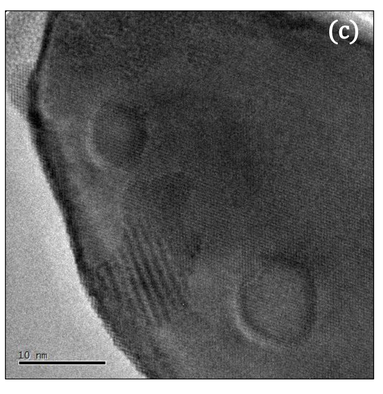


Figure 3 (a, b). SAED's of β-U_3O_7 showing ordered series of satellite reflections, commensurate with the basic structure.

Figure 3 (c). Bright field high-resolution image of a single grain (O/U = 2.32) showing epitaxial growth of a higher uranium oxide on the surface.

Kinetics of UO_2 oxidation

Extent of oxidation is controlled by **(1)** specific surface area, **(2)** temperature, **(3)** oxygen availability and **(4)** time.

Multiple stages considered:
1. Chemi- and physisorption of oxygen
2. Diffusion (or electrostatically induced movement) of oxygen through oxidized surface layer
3. Nucleation-and-growth of a higher oxide, see Figure 3 (c)

Discussion

- The uranium oxides are mixed-valence compounds ($U^{4+} \rightarrow U^{5+}$/ U^{6+}), a feature which still requires additional analysis
- Complex crystallographic changes occur in compounds with O/U > 2.25: modulated structures
- The formation of an oxidized surface layer has not been confirmed, more likely the mechanism involves the epitaxial growth of higher oxides

Conclusion

The mechanism of UO_2 oxidation is concerned mostly with changes in the anion sublattice up to the composition O/U ≈ 2.33

→ The fluorite UO_2 structure serves as a *parent* for the intermediate oxides β-$U_4O_{9\pm y}$ and β-U_3O_7 (Figure 4)

→ Understanding the crystal structures of these oxides improves models for U_3O_8 formation

Powder pyrophoricity is a consequence of the highly exothermic reaction between oxygen and a freshly reduced surface of UO_2

→ Reduction in specific surface area, environmental temperature and oxygen partial pressure

→ Passivation of particle surface by appropriate thermal treatment

} **Pyrophoricity risk ↓**

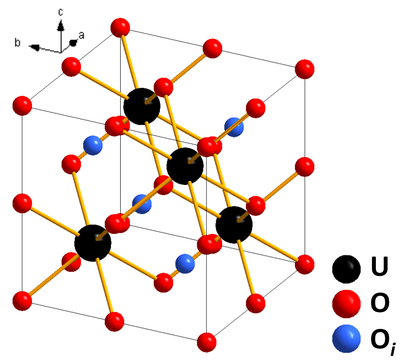


Figure 4. Fluorite structure of UO_{2+x}.

[1] G. Leinders *et al.*, *J. Nucl. Mater.* **2015**, *459*, 135
[2] L. Lynds *et al.*, in *Nonstoichiometric Compounds, Vol. 39*, American Chemical Society, **1963**, pp. 58.
[3] R. I. Cooper and B. T. M. Willis, *Acta Crystallogr. A* **2004**, *60*, 322.